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COMPOSITION AND STRUCTURE OF THIN QUARTZ FILMS ON METALS (A REVIEW)

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X-ray electron spectroscopy and atomic force microscopy methods are used to investigate thin quartz films on steel and copper obtained by silicon cathode spraying in oxygen. The kinetics of film formation is investigated.

Interest in the structure of thin quartz films is due to their wide use in microelectronics for passivating surfaces and protecting large integrated circuits, memory elements, etc.

The purpose of this study was to investigate the composition and structure of thin quartz films on steel and copper using the methods of x-ray electron microscopy and atomic force microscopy. Thin SiO_2 layers were produced in a vacuum chamber by cathode spray deposition of silicon in oxygen at room temperatures. Steel was used as a substrate. Before depositing films, substrates were polished and degassed under heating (250°C) in vacuum at about 10^{-6} Pa. X-ray spectra were recorded with a ÉS-2401 modernized electron spectrometer. Vacuum in the preparation chamber was 10^{-7} Pa, and in the energy analyzer chamber 5×10^{-8} Pa. Spectra were excited by MgK_α radiation. The spectra were calibrated based on the C1s line from the adsorbed hydrocarbon layer with a bond energy $E_b = 285.0$ eV. The surface was purified from the adsorbed impurity layer by argon ionic bombardment (950 eV).

Complex x-ray-electron spectra were decomposed using the Fourier fast discrete transform method with an improved convergence procedure was used. The surface topography was investigated using a PMSPM-MDT scanning probe microscope made by HT MDT company (Russia). Silicon cantilevers with a needle curvature radius less than 10 nm and a vertex convergence angle of the needle equal to 20° were used. Contact measurement of topography were preformed in air.

X-ray diffraction analysis was performed on a DRON-3 diffractometer with CuK_α radiation and a carbon monochromator, and mass-spectrometric analysis was performed on a MS-7201 spectrometer using argon ions (4.5 keV); pickling rate was 40 Å/min and vacuum was 10^{-6} Torr of mercury column.

Massive vitreous quartz. The structure of vitreous quartz and various modifications of crystalline quartz has been investigated in sufficient detail by direct structure-sensitive methods; x-ray diffraction analysis, positron annihilation, and electron microscopy. According to theses studies, the main structural unit is the $[SiO_4]$ tetrahedron. Tetrahedrons are united in rings and chains, whose sizes depend on the modification of quartz [1 – 3]. Short-range ordering in vitreous quartz in general coincides with ordering in crystalline modifications, i.e., the $[SiO_4]$ tetrahedron is preserved as a structural unit. Tetrahedra are mostly joined into 5- and 6-member rings [1, 4].

There are two types of oxygen atoms in the structure of crystalline α-SiO_2: bridge (between two silicon atoms) and end oxygen (– Si = O). The distance $d(Si - O_{br}) = 1.666$ nm, and $d(Si - O_{end}) = 1.602$ nm. The Si – O – Si angle is equal to 143.69°. As the structure of silicon oxide changes, the Si – O – Si angle and the Si – O bond length vary in correlation: a decrease in the bond length is accompanied by an increasing angle. In this case the size of silicon-oxygen rings and the density of the modification grow [1, 2, 5].

The Si – O mean bond length in quartz glass is close to the bond length in α-SiO_2 (1.62 Å). Due to the absence of long-range ordering in the arrangement of tetrahedrons, the Si – O – Si angle changes within an interval of 120 – 180° with a mean value of 144° [6].

X-ray electron studies of quartz are scarce [7 – 10]. The bond energy of O1s and Si2p lines reported by various authors and obtained in our experiments differ (Table 1). We believe that this is related to different spectra calibration methods or to charge compensation.

Any sample brought into vacuum from the atmosphere has a contaminating adsorbate layer on its surface. After decomposition of O1s spectrum obtained on a ÉS-2401 spectrometer in our study, three components were isolated with bond energy of 532.3 eV (23%), 533.3 eV (69.2%), and

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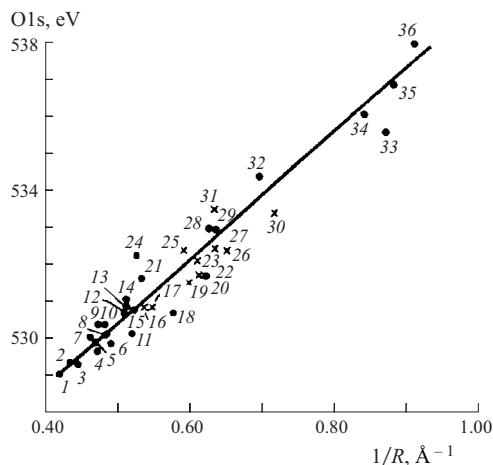
Fig. 1. Correlation of the bond energy of O1s electrons and reverse value of interatomic distance: *1*) La_2O_3; *2*) CdO; *3*) CeO_2; *4*) PbO_2; *5*) In_2O_3; *6*) NiO; *7*) ZrO_2; *8*) MgO; *9*) ZnO; *10*) CoO; *11*) TiO_2; *12*) Nb_2O_5; *13*) SnO_2; *14*) MoO_3; *15*) CuO; *16*) Li_2SeO_3; *17*) $LiIO_3$; *18*) V_2O_5; *19*) Li_3PO_4; *20*) Li_2SO_4; *21*) Al_2O_3; *22*) BeO; *23*) Li_2SO_3; *24*) GeO_2; *25*) $LiBrO_3$; *26*) $LiClO_3$; *27*) Li_2CO_3; *28*) SiO_2; *29*) B_2O_3; *30*) $LiNO_3$; *31*) $LiClO_4$; *32*) SO_2; *33*) CO_2; *34*) NO_2; *35*) CO; *36*) NO.

534.3 eV (7.6%). The high-energy low-intensity component correlates with oxygen which forms part of the adsorbed layer. The amount of impurities depends on the type of sample. The surface of quartz is relatively passive: adsorbed water molecules and OH^- group are virtually completely removed in high vacuum at a temperature of 300 K [15]. Ionic purification decreases the contribution of this component up to its complete disappearance after 10 – 15 min of treatment. It is known [4] that protracted ionic bombardment may disturb the composition and structure of vitreous quartz. Therefore, Table 1 shows the spectra parameters obtained in the present study after 3-min purification of surface.

The authors in [16] did not perform mathematical processing of quartz spectra believing the line O1s to be an individual line. We decompose these spectra, as a consequence of which two components with an energy distance of 1.5 eV were isolated. The intensities ratios of low- and high-energy components of oxygen in the O1s spectrum obtained in out experiment are close to the vitreous quartz spectrum reported in [16].

Analysis of experimental studies of oxides and oxygen-bearing inorganic compounds of different elements established that the position of O1s line correlates with the value *d* of the E – O interatomic distance: the increase in the bond energy of O1s electrons is directly proportional to the reverse value of interatomic distance (Fig. 1) [17]. A correlation of positions of high- and low-energy components of O1s spectra makes it possible to attribute the high- and low-energy component to the end and bridge oxygen atoms, respectively. Analysis of the spectra in [16] shows that the relative quantity of bridge oxygen in vitreous quartz (E_b(O1s) = 531.2 eV) is nearly twice as much as in crystalline modifications (E_b(O1s) = 530.6 and 530.9 eV). The values *d* obtained from our spectra are nearer to the values of interatomic distances determined by structure-sensitive methods [1] than the values obtained on the basis of energy bond of O1s in [16]. This suggests that our calibration of spectra is correct (Table 1).

The Si2p spectra have the characteristic appearance of an unresolved doublet. The nucleus for decomposition is a doublet with a 2 : 1 intensity ratio of the component lines [18] and an energy interval between the doublet components $\Delta\varepsilon$ = 0.68 eV. The value $\Delta\varepsilon$ found by us in the decomposition of the Si2p spectrum of pure silicon agrees with experimental results obtained from spectrum Si(111) excited by monochromatic MgK_α radiation [10]. The Si2p spectra of vitreous quartz indicate the presence of two states of silicon atoms with Si2p bond energy 102.4 and 103.2 eV. The intensity ratio of the low and high-energy components in the Si2p spec-

TABLE 1

Sample	Si2p lines			O1s lines			d(E – O),* Å	Published source
	$E_{b\,max}$, eV	E_b of components, eV	relative content, %	$E_{b\,max}$, eV	E_b of components, eV	relative content, %		
Vitreous quartz	533.3	532.3	23.2	103.2	103.2	71.2	1.79	Data of the
		533.3	69.2		104.2	28.8	1.67	present study
		534.3	7.6				1.54	
		533.0	–	–	103.3	–	–	–	[11]
		532.5	532.5	100.0	103.4	103.4	100.0	1.75	[12]
		532.3	532.2	59.9	–	–	–	1.79	[13]
		532.7	40.1	–	–	–	1.72	
		532.4	531.2	26.2	–	–	–	1.96	[14]
		532.4	73.8	–	–	–	1.79	
α-SiO_2	–	530.6	14.6	–	–	–	2.02	[14]
		532.1	85.4	–	–	–	1.79	
Cristobalite	–	530.9	13.0	–	–	–	1.90	[14]
		532.5	87.0	–	–	–	1.75	

* Based on data in Fig. 1.

trum is close to the intensity ratio of the bridge and the end oxygen in the O1s spectrum.

According to the crystalloid model of silicate glass structure, the glass structure is represented by a stereometrically determined arrangement of crystalloids linked in a unified structure [16]. A crystalloid is a seed (fragment) of a crystalline structure consisting of a group of atoms connected to each other according to the stereometric ordering rules inherent in one of the polymorphous modifications of the material, except for the rule of translational symmetry of crystals. The notion of a crystalloid is directly related to the concept of "intermediate-range ordering," which is a stereometrically determined combination of short-range orderings within the crystalloid. Stereometrically ordered crystalloids of different polymorphic modifications unite in accordance with the ordering rules of one of these polymorphous modifications (except for the translational symmetry rule), but due to statistical alternation of different short-range and medium-range orderings inherent in them they form a disordered polymer polymorphic-crystalloid vitreous material structure, in which ordering and disordering organically coexist. In contrast to crystalline materials, long-range ordering is absent in glasses [16].

Figure 2 shows an ACV-image of a quartz fracture. The fracture surface is uniformly covered by facets in the form of nearly regular pyramids of size 2500 Å and height 200 Å. The regular structure of the surface suggests that it has a crystalline structure. Reflections indicating the presence of crystalline phases are not found in the x-ray pattern of massive vitreous quartz. It was assumed that these reflections would be registered on x-ray patterns of mechanically crushed quartz, i.e., when the surface area increased. However, milled quartz as well was found to be x-ray amorphous. This suggests that the regularly arranged pyramids on the fracture surface of vitreous quartz are not the results of surface crystallization, but a reflection of a polymorphous-crystalloid structure of the sample volume. This assumption is further corroborated by the fact that the size of the pyramidal structures on the surface are comparable to the sizes of crystallite-like areas in the volume, in which they are estimated at about 1700 Å [19].

Thin SiO_2 *films*. X-ray-electron analysis of SiO_2 films was performed in [20]. The films were obtained by oxidation of silicon and monosilane. An attempt was made to estimate the value of the $Si - O - Si$ angle in the silicon-oxygen anions based on the value of the Si2p line displacement ΔE_b in SiO_2 films (of thickness several tens of angstroms) compared with the position of the Si2p line in pure silicon. The film structure was not investigated by other methods. The relationship between the value of the charge transferred from the silicon atom to the oxygen atom Δn per one $Si - O$ bond and
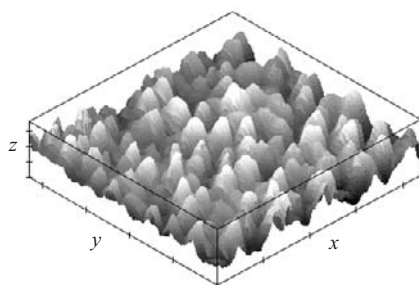

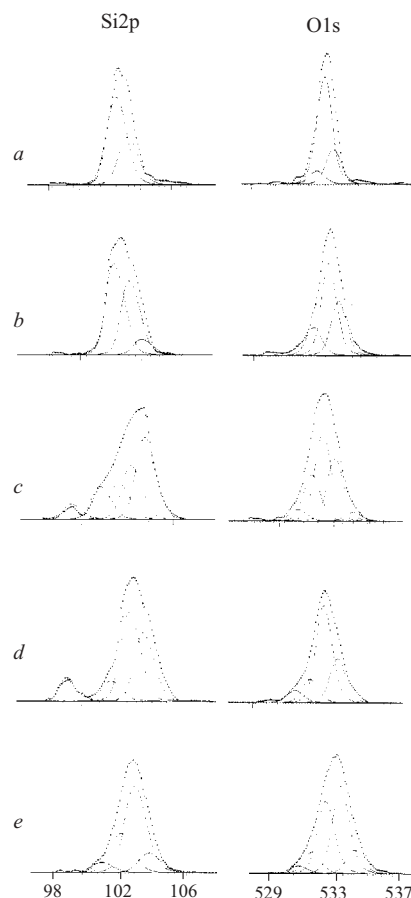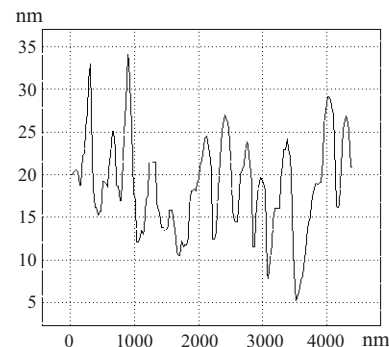**Fig. 2.** Fracture of vitreous quartz.

Fig. 3. X-ray electron spectra of SiO_2 films: *a*, *b*, *c*, and *d*) thickness equal to 3000, 1000, 500, and 200 Å, respectively; substrate – steel; *e*) thickness 200 Å, substrate – copper.

the value of the angle $Si - O - Si$ was theoretically calculated (Fig. 3): Δn and ΔE_b grow with increasing angle.

Correlating the values of angles $Si - O - Si$ and ΔE_b of the line Si2p in different crystalline phases of silicon with the size of silicon-oxygen rings, the authors in [20] conclude that the film structure contains $4 - 8$-member rings. However, it is known that substantial compressive stresses are present in films, which are similar to a pressure effect [21]. It was es-
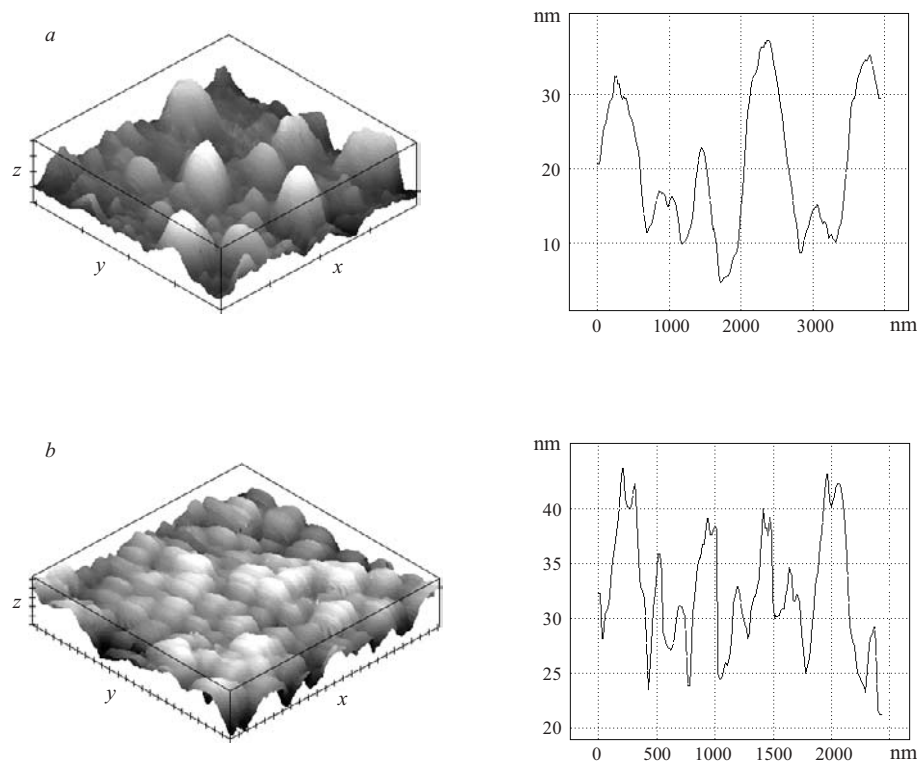
Fig. 4. Vitreous quartz film on steel substrate: *a* and *b*) film thickness equal to 500 and 1000 Å, respectively.

tablished by the x-ray diffraction method that as the density of vitreous quartz increases by 16% under the effect of pressure, the Si – O and O – O distances do not change, whereas the Si – Si distance decreases (although insignificantly) and, as a result, the Si – O – Si angle decreases by about 5%. The decrease in the mean value of the angle may occur by two ways: by an increasing content of small rings or by a deformation of large rings. The second way is the more probable [22]. Consequently, it is impossible to estimate the size of silicon-oxygen anions in silicates based only on data on variation of the Si – O – Si angle. These data can only indicate variations in the silicate structure density.

The authors in [11] formulated a concept of polymorphism of glasses, according to which two condense amorphous phases of the same chemical composition, differing in their structure, tetrahedron orientation angle, and Si – Si and O – O distances can coexist in equilibrium in a vitreous state. Coexistence of two different amorphous phases with separation boundaries identified as areas of size 500 – 1000 Å using small-angle x-ray scattering and electron microscopy was observed. The phase with the shorter Si – Si distances is named metallict. This is a sufficiently stable phase, which transforms into the usual quartz glass only after several hours of exposure at a temperature of 1370°C. The presence of two amorphous phases differing in specific volumes is presumably typical of one-component systems. The phase transformation of the first kind from one amorphous phase into another was observed experimentally under a pressure increase

up to several GPa. The structure of films obtained by vacuum spraying repeats the structure of the metallict phase [14].

The relative quantity of the metallict phase in massive quartz is insignificant; therefore, a component corresponding to this denser modification was not isolated in the Si2p spectra of massive quartz.

It is known [12] that the microstructure of thin amorphous and crystalline (metallic, semiconductor, dielectric) films is acicular and can be described as a lattice of a decreased density enclosing elevated density areas of size 5 – 200 Å. An acicular structure of higher-density areas in films about 500 Å thick has been proved experimentally. High-density areas consist of mutually parallel cylinders which are formed at the angle of spraying. The reasons for acicularity lie in the self-shading mechanism in film growing and in the limited mobility of particles spray-deposited on a substrate. The stage of formation of seed columns is obligatory in any process of film precipitation and such film structure may persist up to a thickness of 4000 Å.

It can be seen in Fig. 4 that film 500 Å thick was formed from primary seeds of a nearly spherical shape with a diameter about 1000 Å Primary seeds were uniformly located over the surface and in melting formed a continuous film with a total thickness of 1000 Å.

Table 2 shows the parameters of x-ray-electron O1s and Si2p spectra of silicon dioxide films on a metal substrate. The substrate material composition was analyzed using the secondary mass- spectrometry method (atomic content, %):

88.45 Fe, 9.45 Cr, 1.68 Al, 0.42 Ti. Heating of the substrate in vacuum for degassing produces modifications in the surface composition directly adjacent to the SiO_2 film, i.e., results in week enrichment of surface with aluminum and intense enrichment with titanium. Titanium and aluminum are metals whose free energy of oxide formation is lower than that of SiO_2; therefore, they can directly reduce silicon dioxide with formation of pure silicon, silicides, and metal oxides [13]. The position of the low-energy component correlates with the analogous position of pure silicon and silicon in $TiSi_2$ compound. This component is missing in the Si2p spectrum of film 200 Å thick deposited on copper, since the free energy of copper oxide formation is higher than that of silicon dioxide [13]. The peaks at 102.3, 103.3, and 104.3 eV correlate with $Si - O - Si$ bonds that have different angles. The first two peaks were observed as well in spectra of massive vitreous quartz. The high-energy peak points to the presence

TABLE 2

Sample thickness, nm	Si2p spectrum			O1s spectrum			$d(E-O)$,[*] Å
	$E_{b\,max}$, eV	E_b of components, eV	relative content, %	$E_{b\,max}$, eV	E_b of components, eV	relative content, %	
3000	103.1	102.4	64.6	532.5	531.8	8.1	1.87
		103.2	35.4		532.3	69.0	1.79
					533.1	22.5	1.69
1000	103.1	102.2	50.3	532.5	531.4	16.2	1.92
		103.2	41.0		532.3	52.5	1.79
		104.1	8.7		533.1	31.2	1.69
500	104.1	99.3	6.8	532.5	530.4	5.3	2.08
		101.3	14.9		531.5	20.3	1.90
		102.4	16.6		532.3	40.0	1.79
		103.2	24.4		533.1	30.0	1.69
		104.1	37.2		534.4	4.1	1.54
200	104.0	99.2	11.5	531.9	530.1	6.8	2.14
		102.0	10.0		531.2	13.1	1.95
		103.3	44.5		532.2	55.4	1.79
		104.2	34.0		533.2	24.7	1.67
200[**]	103.3	101.1	6.4	533.0	530.2	3.4	2.13
		102.3	25.2		531.1	9.6	1.96
		103.2	55.8		532.2	34.5	1.79
		104.2	12.5		533.2	42.0	1.67
					534.3	10.5	1.54

[*] Data in Fig. 1.

[**] On copper.

of areas with a higher density. It can be assumed that it correlates with the metallict phase, whose relative content in the films is high. The peak of 101.2 eV is typical of aluminum and iron silicates. The absence of the peak of 99.2 eV in the film spectra 1000 and 3000 Å thick is due to the fact that the film – alloy boundary is outside the analyzed layer.

The position of the components of Si2p spectrum of film of thickness 3000 Å correlates with the position of the components of Si2p spectrum of the sample fracture, whereas their intensity ratios differ. This can be attributed to the difference in the structure of silicon-oxygen anions: the effect of structures with smaller $Si - O - Si$ bond angles in the film increases.

The high-energy component with bond energy of 534.3 eV in the O1s spectrum relates to oxygen of the adsorbed impurity layer. The low-energy component correlates with oxygen bonded to the substrate metals (oxides, silicates). The element – oxygen distances indicated in Table 2 were obtained on the basis of data from Fig. 1. The values $d = 2.1 - 2.3$ Å are typical of metal oxides (FeO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO, and TiO_2). These distances in metal silicates are shorter.

Thus, the vitreous quartz structure contains two forms of oxygen differing in the silicon- oxygen bond length and two types of silicon atoms, which points to the existence of silicon-oxygen structures with different values of $Si - O - Si$ angles.

The fracture surface of massive amorphous quartz contains regularly located nearly regular pyramids of size

2500 Å and height 200 Å. No crystallization is observed on the surface of vitreous quartz in fracture. The fracture topography reflects the volume structure, i.e., uniform alternating of areas with the same intermediate-range ordering.

The structure of thin quartz films on metal substrates obtained by spraying in vacuum at room temperature is formed by the mechanism of seed formation and can be described as acicular.

Analysis if the Si2p spectrum suggests that the structure of films not greater than 1000 Å thick contains silicon-oxygen anions with $Si - O - Si$ angles that are equal to the angles existing in massive vitreous quartz, and rings whose $Si - O - Si$ angles are larger than those in vitreous quartz. The presence of the latter indicates that there are areas whose density is somewhat higher than in massive vitreous quartz.

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